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Abstract. Hot gas clean-up (HGC) technology uses special zinc oxide based sorbents. Sorbent attrition is one of the negative factors that should be improved. The current study has determined that one of the main reasons of sorbent reduction is interaction with syngas components, namely, carbon monoxide, hydrogen, methane and carbon (side reactions). In this study, kinetics of main reaction (h2s adsorption by zinc oxide) and side reactions were considered and compared. Models of chemical processes and mechanisms were considered as well. Complicated nature of HGC process was researched. It is stated that the process can run in three different phases (gas, solid, dust). Methods of TGA data calculation are presented and compared with literature. In syngas where hydrogen sulphide concentration is much lower than concentration of hydrogen and carbon monoxide, main reaction is dominant at temperatures near 300–500 °C. At 650 °C main reaction takes the second place after H_2 reduction, and at 850°C it is the third after CO reduction (with diffusion resistance of product shell). Hydrogen reduction is more active than carbon monoxide reduction, that is why CO/H_2 ratio in syngas should be increased for rising the HGC operation temperature. A wide range of processes (main and side reactions) was considered with the use of the same materials, equipment and methods.

1. Introduction

Hot gas clean-up (HGC) can become a part of next generation of IGCC. HGC technology was successfully tested on Polk Power Station in pilot regime. HGC technology uses special zinc oxide based sorbents. Sorbent attrition is one of the negative factors that should be improved. The current study has determined that one of the main reasons of sorbent reduction is interaction with syngas components. Syngas desulfurization is realized with the use of zinc oxide based sorbents. The main reaction is hydrogen sulfide adsorption by zinc oxide. Side reactions are reductions of zinc oxide in carbon monoxide, hydrogen, methane and carbon. Main reaction (table 1) was researched in [1 - 8]. Kinetics of side reactions was studied in: [8, 9] for hydrogen, [10] for carbon monoxide, [11, 12] for methane and [13, 14] for carbon. Main reaction is a reaction of replacement; zinc oxide in sorbent converts into a solid shell of zinc sulfide. Physical properties of sorbents, e.g., diffusion resistance of the shell and specific surface area were studied in [15].

Table 1. Process reactions

#	Reaction	#	Reaction
1	$ZnO^S + H_2S^g \rightarrow ZnS^S + H_2O^g$	4	$ZnO^S + CO^g \rightarrow Zn^S + CO_2^g$
2	$ZnO^S + H_2^g \rightarrow Zn^S + H_2O^g$	5	$ZnO^S + C^d \rightarrow Zn^S + CO^g$
3	$ZnO^S + CH_4^g \rightarrow Zn^S + CO^g + 2H_2^g$		

According to literature, zinc oxide based sorbents are not stable in syngas atmosphere, that is why proper simulation of HGC process needs input data on side reaction kinetics. The goal of current study was to compare influences of main and side reactions on zinc oxide based sorbent for HGC reactor in similar conditions and the objectives were as follows:

1) to carry out TG experiments with zinc oxide based sorbent and main syngas components (hydrogen sulfide, hydrogen, carbon monoxide, methane and carbon) and to determine kinetic constants of reactions;

2) to run a simulation, based on determined kinetic constants, of main and side reactions (rate of reactions) in temperature range 300 - 850 °C taking into account macrokinetic limitations.

2. Models and methods

2.1. Heterogeneous reaction of replacement

Mass transfer in porous sorbent body was described with the use of grain model. Surface are of porous body is a sum of spherical grain surfaces. Grains have similar size and physical properties.

2.1.1. Core (Kinetics)

Reaction rate on the core surface according to the mass action law for heterogenic reactions can be described as

$$R = k \cdot C_c^{n_1} \cdot S_c \cdot N_g \tag{1}$$

$$k = k_{so} \exp\left[-\frac{E}{RT}\right] \tag{2}$$

where pre-exponential factor for kinetics and kinetic energy activation are kinetic constants that have to be determined during TG experiments and raw data calculation.

2.1.2. Shell (Diffusion)

Mass flux through the product shell is

$$R = \frac{1}{O_{sh}}\left(C_{sh} - C_c\right)N_g\,, \tag{3}$$

Where C_{sh}, C_c mole/m^3 - are the gas concentrations on particle surface and on core surface.

Mass transfer coefficient is

$$\frac{1}{O_{sh}} = D_{sh}\frac{4\pi}{\frac{1}{r_c} - \frac{1}{r_{sh}}}. \tag{4}$$

2.1.3. Mass transfer (Macrokinetics)

If reaction order is 1, mass transfer equation can be transformed

$$R = \frac{1}{\frac{1}{k \cdot S_c} + O_{sh}} C_{sh} N_g\,. \tag{5}$$

Grade of J&M Katalco 32-4 grade sorbent was crashed and sieved (50-100 μm). Crashed sorbent with a sample mass was tested in TG analyzer NETZSCH STA 449F3 in transient regime (temperature range 300 - 850 °C). Temperature increase was different: 20 k/min for main reaction and 15 K/min for side reactions. More detailed information about experiments was published in [3].

2.2. Calculation of kinetic constants of main reaction

Dependence $k = f(t)$ was found from equation (10) at fixed temperature. This dependence let to find kinetic constants (pre-exponential factor and energy activation) by linearization of $k = f(t)$.

2.3. Calculation of side reactions kinetic constants

Calculations are based on equations (1)-(5). Diffusion constants (D_{so}, E_D) are among initial parameters. Mass flow rate G was taken from TGA curve, as a relation between mass difference and time difference.

3. Results

3.1. Kinetic constants determination

Kinetic constants were calculated from our experimental data with the use of current methods. Our results were compared with data from literature. It can be seen that our results are closer to [10] (figure 2a). Hydrogen sulfide adsorption by zinc oxide is the main reaction in HGC process. Solid product zinc sulfide shell forms on the core of zinc oxide in the sorbent during this reaction. Approximation in figure 2a refers to author's calculations. It correlates with [4. 5, 8] calculated by method from current study and original [10]. Original data from [3, 6] (figure 2a) do not correlate with [10], that was noted in [4]. Results from [7, 9] calculated by current method do not correlate with [10] too. Approximation figure 2b refers to author's data, and calculation of [10, 11] by current method correlates with original data.

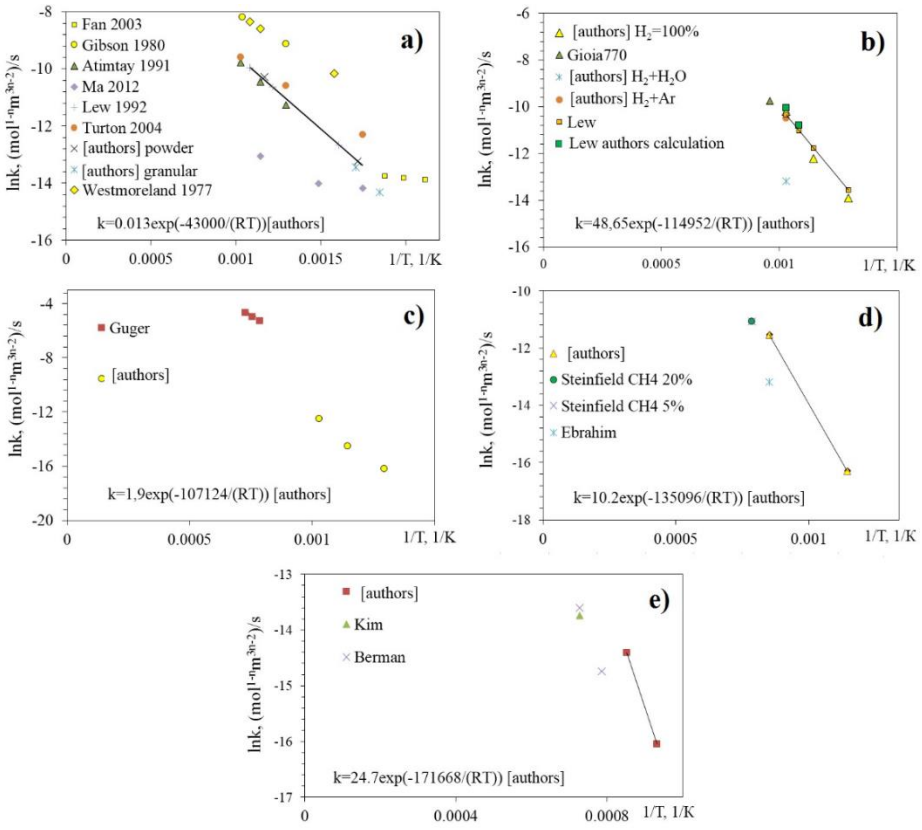

Figure 1. Temperature dependence on reaction rate constant in Arrhenius coordinates a) hydrogen sulfide b) hydrogen c) carbon monoxide d) methane e) carbon.

Reaction rate constant depends on temperature and composition of components and does not depend on gas concentration (it can be seen from figures 2a-2e, because gas concentrations in all experiments were different). One of the most probable and destructive side processes is hydrogen reduction (figure 2b) with metallic zinc formation (if temperature is higher than 400 °C). It has the widest range of influence in temperature scale. Active stage of sorbent destruction starts at 650 °C.

Carbon monoxide is the second main syngas component that can play crucial role in sorbent destruction. Kinetics of carbon monoxide reduction is presented in figure 2c. Approximation of author's experimental data is shown in figure 2c and it doesn't correlate with data from [12]. However, original approximation from [12] and the approximation of it with current method are the same. Methane volume fraction in syngas is less than 2 %. The reaction was detected at 850 °C. The reaction order for methane reduction was 0.68.

Non-availability of wet scrubbing in HGC may be the reason of carbon fines injection in HGC reactor. Reaction activity was detected at 800 °C (figure 2e).

3.2. Comparison of reaction rates

Different orders of reaction make comparison of reaction rate constants impossible because of different units. The reaction rate has universal units (mole of component per second), though the method of reaction activity comparison is based on reaction rates. The method allows determining the reaction rate by reaction rate constants, that could be taken from literature or from experimental results. It is necessary to mention that comparison should be conducted in special conditions. First of all gas component concentrations should be taken from real cases (in our study we put Polk Power Station syngas composition [1]. Equal diffusion conditions are one more factor. Side reactions of ZnO reduction do not have any shell of product (zinc sulfide shell on the surface of zinc oxide core), but in real cases sorbent will have shell of ZnS product because of main reaction influence. Hence syngas components, e.g., CO and hydrogen will diffuse through this shell, and this process may change the rate of reaction, so this effect should be taken into account. The last condition is residence time τ^* of gas in sorbent should be equal for all reactions.

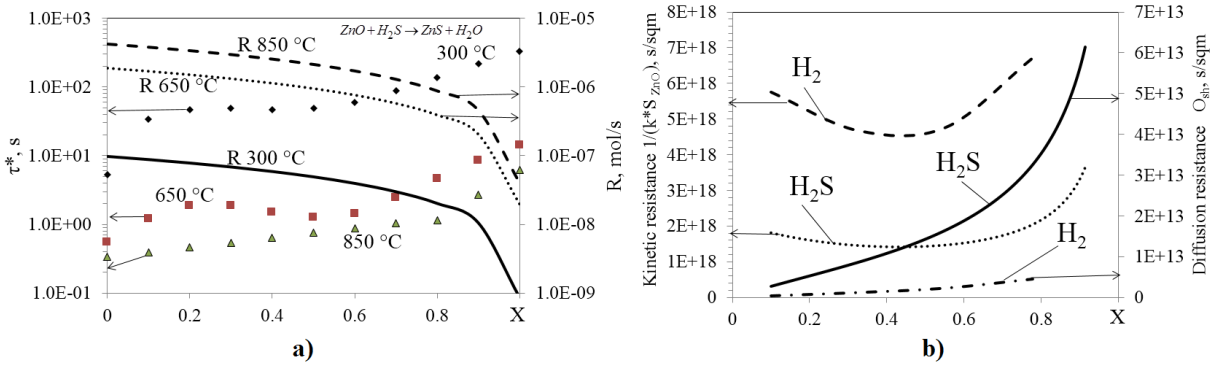

Figure 2. Functions of a) residence time, rate of reaction b) kinetic and diffusion resistance of conversion.

The activity of sorbent (the rate of reaction) falls with conversion rise, though residence time of gas should be higher to reach full purification of syngas (figure 3a). It can be seen that diffusion resistance of hydrogen sulfide through the shell is much higher than the same parameter for hydrogen, but it

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doesn't have any influence on reaction rate because both diffusion resistances are much less that kinetic resistances (figure 3b).At the first step we do not take into account the chemical interaction between main and side reactions, and we determine basic rate of reactions, generally written as R. Rate of reaction for multiple reactions can be calculated as

$R^*_{H_2S} = rf_{H_2S}(t, X) \cdot R_{H_2S}$, where rf_{H_2S} – is the selectivity (for main reaction in this case)

$$rf_{H_2S} = \frac{R_{H_2S}}{R_{H_2S} + R_{H_2} + R_{CO}}$$

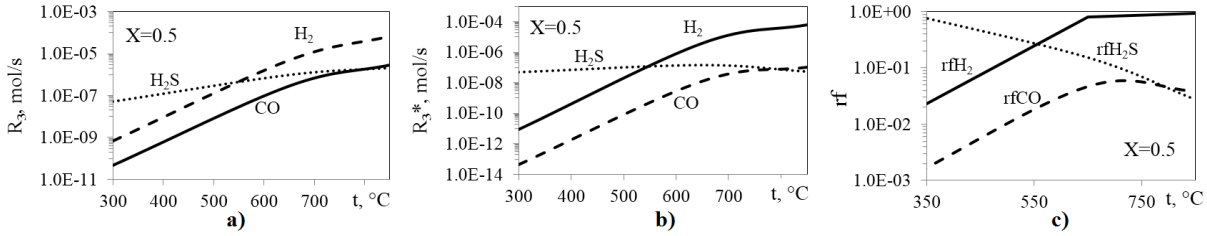

Figure 3. Comparison of functions a) rate of reaction without selectivity influence b) rate of reaction with selectivity influence c) selectivities of temperature.

Main reaction is dominant up to 550 °C; afterwards the hydrogen reduction takes first place, then at a temperature of 800 °C main reaction falls down on third place after carbon monoxide reduction (figure 3a). The same happens with selectivities (figure 3c). The selectivity influence is seen to increase the difference between reaction rates, while all control points do not change.

Conclusion

Kinetic characteristics of used sorbents were closer to [8] rather than to [4]. Kinetic data of side reactions in missed temperature ranges has been studied. HGC materials were used. All the experiments were conducted with the same materials for both main and side reactions

Comparison of reaction rates shows that the main reaction in HGC process for gas composition from table 3 is dominant in temperature range 300 - 550 °C. Hydrogen is shown to be the most active component in syngas, though its concentration reduction in syngas composition (H_2/CO reduction) can make the working temperature range of HGC wider.

Nomenclature

C_{sh}, mole/m^3 - gas component concentration on the solid product shell

C_c, mole/m^3 - gas component concentration on the core

D_{sh}, m^2/s - diffusion coefficient

D_{so}, m^2/s - diffusion pre-exponential factor

E, J / $mole$ - kinetic energy activation

E_D, J/mole - diffusion energy activation

k_{so}, $\frac{mole^{1-n} \cdot m^{3n-2}}{s}$ - pre-exponential factor for kinetic rate constant

k, -/- - kinetic rate constant;

n - reaction order

N_g - number of grains

O_{sh} - shell diffusion resistance

R, mole/s - reaction rate for real syngas concentrations with no selectivity

rf - selectivity

R^*, mole/s - reaction rate for real syngas concentrations with selectivity

r_c, m -core radius

r_{sh}, m - shell radius

S_c, m^2 - core surface area

t, °C - temperature

X - conversion

τ^*, s - gas residence time in reactor

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